Molecular Dynamics Studies of Concentrated Binary Aqueous Solutions of Lanthanide Salts: Structures and Exchange Dynamics

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Concentrated binary aqueous solutions of lanthanide (Nd^{3+} and Dy^{3+}) salts (ClO_4^-, Cl^-, and NO_3^-) have been studied by means of classical molecular dynamics (MD) simulations with explicit polarization and UV−visible spectroscopy. Pair interaction potentials, used for the MD simulations, have been developed in order to reproduce experimental hydration properties. Nd^{3+} and Dy^{3+} have been chosen because of their position in the lanthanide series: Nd^{3+} being a light lanthanide and Dy^{3+} a heavy one. They are respectively coordinated to nine and eight water molecules, in pure water, involving changes in their salt hydration structures. Both MD simulations and UV−visible experiments highlight the stronger affinity of nitrate anions toward Ln^{3+} compared to perchlorates and chlorides. Dissociation/association processes of Nd^{3+}−Cl^- and Nd^{3+}−NO_3^- ion pairs in aqueous solution have been analyzed using potential of mean force profile calculations. Furthermore, from MD simulations, it appears that the affinity of anions (perchlorate, chloride, and nitrate) is stronger for Nd^{3+} than Dy^{3+}.